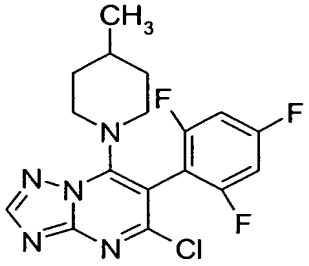
Fungicidal mixtures for controlling harmful fungi

Description

The present invention relates to fungicidal mixtures for controlling harmful fungi, which mixtures comprise, as active components,

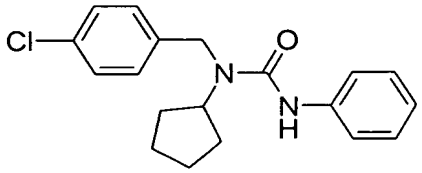
1) the triazolopyrimidine derivative of the formula I



I

and

2) pencycuron of the formula II



II

in a synergistically effective amount.

Moreover, the invention relates to a method for controlling rice pathogens using mixtures of the compound I with the compounds II and to the use of the compound I with the compounds II for preparing such mixtures, and to compositions comprising these mixtures.

The compound I, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, its preparation and its action against harmful fungi are known from the literature (WO 98/46607).

The compound II, 1-(4-chlorobenzyl)-1-cyclopentyl-3-phenylurea, its preparation and its action against harmful fungi are likewise known from the literature (Mitt. Biol. Bundesanst. Land-Forstwirtsch., Berlin-Dahlem, Vol. 203, p. 230 (1981); DE 27 32 257; common name pencycuron).

Mixtures of triazolopyrimidines with other active compounds are known from EP-A 988 790 and US 6 268 371.

The synergistic mixtures disclosed in EP-A 988 790 are described as being fungicidally active against various diseases of cereals, fruit and vegetables, such as for example mildew on wheat and barley or gray mold on apples. The mixtures disclosed in US 6 268 371 are described as being fungicidally active, in particular against rice pathogens.

It is an object of the present invention to provide, with a view to an effective control of harmful fungi, in particular rice pathogens, at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, have an improved activity against harmful fungi.

The mixtures defined at the outset have accordingly been found. Moreover, we have found that with simultaneous, that is joint or separate, application of the compound I and the compound II or successive application of the compound I and the compound II, better control can be exerted over harmful fungi than is possible with the individual compounds (synergistic mixtures).

The mixtures of the compound I and the compound II or the simultaneous, joint or separate, use of the compound I and the compound II are distinguished by being highly active against a wide range of phytopathogenic fungi, in particular from the classe of the *Ascomycetes*, *Deuteromycetes*, *Oomycetes* and *Basidiomycetes*. They can be used in crop protection as foliar and soil-acting fungicides.

They are particularly important in the control of a multitude of fungi on various cultivated plants, such as bananas, cotton, vegetable species (for example cucumbers, beans and cucurbits), barley, grass, oats, coffee, potatoes, corn, fruit species, rye, soya, tomatoes, grapevines, wheat, ornamental plants, sugar cane and, in particular, rice, and also on a large number of seeds.

They are particularly important in the control of harmful fungi on rice plants and their seeds, such as *Bipolaris* and *Drechslera* species. They are particularly suitable for controlling rice blast caused by *Pyricularia oryzae*.

In addition, they are also highly effective against a large number of phytopathogenic fungi, such as: *Blumeria graminis* (powdery mildew) on cereals, *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* on cucurbits, *Podosphaera leucotricha* on apples, *Uncinula necator* on grapevines, *Puccinia* species on cereals, *Rhizoctonia* species on

cotton, rice and lawns, *Ustilago* species on cereals and sugar cane, *Venturia inaequalis* on apples, *Bipolaris* and *Drechslera* species on cereals, rice and lawns, *Septoria nodorum* on wheat, *Botrytis cinerea* on strawberries, vegetables, ornamental plants and grapevines, *Mycosphaerella* species on bananas, peanuts and cereals, *Pseudocercosporella herpotrichoides* on wheat and barley, *Pyricularia oryzae* on rice, *Phytophthora infestans* on potatoes and tomatoes, *Pseudoperonospora* species on cucurbits and hops, *Plasmopara viticola* on grapevines, *Alternaria* species on fruit and vegetables and also *Fusarium* and *Verticillium* species.

They can also be used in the protection of materials (e.g. the protection of wood), for example against *Paecilomyces variotii*.

The compound I and the compound II can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

When preparing the mixtures, it is preferred to employ the pure active compounds I and II, to which further active compounds against harmful fungi or against other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers can be added according to need.

Other suitable active compounds in the above sense are in particular active compounds selected from the following groups:

- acylalanines, such as benalaxyl, ofurace, oxadixyl,
- amine derivates, such as aldimorph, dodemorph, fenpropidin, guazatine, iminoctadine, tridemorph,
- anilinopyrimidines, such as pyrimethanil, mepanipyrim or cyprodinil,
- antibiotics, such as cycloheximid, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,
- azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole, dinitroconazole, enilconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tetraconazole, triadimefon, triadimenol, triflumizol, triticonazole,
- dicarboximides, such as myclozolin, procymidone,
- dithiocarbamates, such as ferbam, nabam, metam, propineb, polycarbamat, ziram, zineb,
- heterocyclic compounds, such as anilazine, boscalid, oxycarboxin, cyazofamid, dazomet, famoxadone, fenamidone, fuberidazole, flutolanil, furametpyr, isoprothio-

lane, mepronil, nuarimol, probenazole, pyroquilon, silthiofam, thiabendazole, thifluzamid, tiadinil, tricyclazole, triforine,

- nitrophenyl derivatives, such as binapacryl, dinobuton, nitrophthal-isopropyl,
- other fungicides, such as acibenzolar-S-methyl, carpropamid, cyflufenamid, cymoxanil, diclomezin, diclocymet, diethofencarb, edifenphos, ethaboxam, fentinacetate, fenoxanil, ferimzone, fosetyl, hexachlorobenzene, metrafenone, propamocarb, phthalid, toloclofos-methyl, quintozene, zoxamid,
- strobilurins, such as fluoxastrobin, metominostrobin, orysastrobin or pyraclostrobin,
- sulfenic acid derivatives, such as captafol,
- cinnamides and analogous compounds, such as flumetover.

In one embodiment of the mixtures according to the invention, a further fungicide III or two fungicides III and IV are added to the compounds I and II. Preference is given to mixtures of the compounds I and II with a component III. Particular preference is given to mixtures of the compounds I and II.

The compound I and the compound II are usually applied in a weight ratio of from 100:1 to 1:100, preferably from 20:1 to 1:20, in particular from 10:1 to 1:10.

The components III and, if appropriate, IV are added if desired in a ratio of from 20:1 to 1:20 with respect to the compound I.

Depending on the type of the compound and of the desired effect, the application rates of the mixtures according to the invention are from 5 g/ha to 1000 g/ha, preferably from 50 to 900 g/ha, in particular from 50 to 750 g/ha.

Correspondingly, the application rates for the compound I are generally from 1 to 1000 g/ha, preferably from 10 to 900 g/ha, in particular from 20 to 750 g/ha.

Correspondingly, the application rates for compound II are generally from 1 to 500 g/ha, preferably from 10 to 300 g/ha, in particular from 20 to 200 g/ha.

In the treatment of seed, application rates of mixture of from 1 to 300 g/100 kg of seed, preferably from 1 to 100 g/100 kg, in particular from 5 to 50 g/100 kg, are generally used.

In the control of harmful fungi pathogenic to rice plants, the separate or joint application of the compounds I and II or of the mixtures of the compounds I and II is carried out by spraying or dusting the seeds, the seedlings, the plants or the soils before or after sowing of the plants or before or after emergence of the plants. Application of the com-

pounds is preferably carried out by spraying the leaves. It can also be carried out by applying granules or by dusting the soils.

The mixtures according to the invention, or the compounds I and II, can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular intended purpose; in each case, it should ensure a fine and even distribution of the compound according to the invention.

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries suitable for this purpose are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used,
- carriers, such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers, such as nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates), and dispersants, such as lignosulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenyl ethers, ethoxylated isooctylphenol, octylphenol or nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ethers, tristearylphenyl polyglycol ethers, alkylaryl polyether alcohols, alcohol and fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetals, sorbitol esters, lignosulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or

animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, highly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone or water.

Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers. Examples of solid carriers are mineral earths, such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compounds. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to the NMR spectrum).

The following are examples of formulations:
1. Products for dilution with water

A) Water-soluble concentrates (SL)
10 parts by weight of the active compounds are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

B) Dispersible concentrates (DC)
20 parts by weight of the active compounds are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

C) Emulsifiable concentrates (EC)
15 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). Dilution with water gives an emulsion.

D) Emulsions (EW, EO)

40 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). This mixture is introduced into water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

E) Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of the active compounds are comminuted with addition of dispersants, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

F) Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of the active compounds are ground finely with addition of dispersants and wetters and prepared as water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

G) Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of the active compounds are ground in a rotor-stator mill with addition of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

2. Products to be applied undiluted

H) Dustable powders (DP)

5 parts by weight of the active compounds are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

I) Granules (GR, FG, GG, MG)

0.5 part by weight of the active compounds is ground finely and combined with 95.5% of carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

J) ULV solutions (UL)

10 parts by weight of the active compounds are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions,

powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; they are intended to ensure in each case the finest possible distribution of the active compounds according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. However, it is also possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil which are suitable for dilution with water.

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active compounds may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

Oils of various types, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, even, if appropriate, not until immediately prior to use (tank mix). These agents can be admixed with the compositions according to the invention typically in a weight ratio of from 1:10 to 10:1.

The compounds I and II or the mixtures or the corresponding formulations are applied by treating the harmful fungi or the plants, seeds, soils, areas, materials or spaces to be kept free therefrom with a fungicidally effective amount of the mixture or, in the case of separate application, of the compounds I and II. Application can be carried out before or after infection by the harmful fungi.

The fungicidal action of the compound and of the mixtures can be revealed by the following tests:

The active compounds, separately or jointly, were prepared as a stock solution comprising 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action

based on ethoxylated alkylphenols) was added to this solution, and the mixture was appropriately diluted with water to the desired concentration.

Use example – Protective activity against rice blast caused by *Pyricularia oryzae*

Leaves of rice seedlings of the cultivar "Tai-Nong 67" which had been grown in pots were sprayed to runoff point with an aqueous suspension having the concentration of active compound stated below. The next day, the plants were inoculated with an aqueous spore suspension of *Pyricularia oryzae*. The test plants were then placed in climatized chambers at 22 - 24°C and 95 - 99 % relative atmospheric humidity for six days. The extent of the development of infection on the leaves was then determined visually.

Evaluation is carried out by determining the infected leaf areas in percent. These percentages were converted into efficacies.

The efficacy (E) is calculated as follows using Abbot's formula:

$$E = (1 - \alpha/\beta) \cdot 100$$

α corresponds to the fungal infection of the treated plants in % and

β corresponds to the fungal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants are not infected.

The expected efficacies of the mixtures of active compounds are determined using Colby's formula [R.S. Colby, Weeds, 15, 20-22 (1967)] and are compared with the observed efficacies.

Colby's formula:

$$E = x + y - x \cdot y/100$$

E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b

x efficacy, expressed in % of the untreated control, when using the active compound A at the concentration a

y efficacy, expressed in % of the untreated control, when using the active compound B at the concentration b

Table A – Individual active compounds

Example	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
1	control (untreated)	-	(86 % infection)
2	I	4	31
3	II (pencycuron)	16 1	0 0

Table B – Mixtures according to the invention

Example	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
4	I + II 4 + 1 ppm 4:1	65	31
5	I + II 4 + 16 ppm 1:4	77	31

*) efficacy calculated using Colby's formula

The test results show that, owing to a strong synergism, the mixtures according to the invention are considerably more effective against rice blast than had been predicted using Colby's formula.